

Controlled Growth of Carbon Spheres Through the Mg-Reduction Route

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Received: 9 April 2009 / Accepted: 3 September 2009 / Published online: 19 September 2009
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Abstract Hollow spheres, hollow capsules and solid spheres of carbon were selectively synthesized by Mg-reduction of hexachlorobutadiene at appropriate reaction conditions. X-ray powder diffraction and Raman spectra reveal that the as-prepared materials have a well-ordered structure. A possible formation mechanism has been proposed.

Keywords Chemical synthesis · Carbon · Hollow spheres · Hollow capsules · Solid spheres

Introduction

The emergence of various carbon structures, such as fullerenes, carbon nanotubes and closed spherical carbon shells, has triggered intense interest in this versatile material [1–3]. Various efforts have been made to synthesize different carbon structures and morphologies due to their wide range of applications in semiconductor device, gas storage, nanotweezers and electronics [4–8].

Among carbon structured materials, carbon solid and hollow spheres represent a special class of materials that exhibit unique properties such as low weight, thermal insulation and high compressive strength. Because of these excellent properties, carbon spheres can be applied to many

industrial fields including gas/energy storage adsorbent, support of catalytic systems, electrode material of lithium-ion batteries, encapsulation of products for the controlled release of drugs or cosmetics. [9–11]. Up to now, various approaches have been carried out to prepare hollow and/or solid carbon spheres. For example, Wang and Yin produced graphitic carbon calabashes and solid spheres via a mixed-valent oxide-catalytic carbonization (MVOCC) process at 900–1,050 °C [12]. Kroto et al. reported synthesis of carbon spheres on the large scale by the direct pyrolysis of hydrocarbons [13]. Recently, direct chemical route has been introduced to synthesize carbon materials. Hu et al. synthesized hollow carbon spheres with a self-assembly approach by using hexachlorobenzene and Na as the reactants, the by-product NaCl generated during the reaction had to be removed by annealing the product above 1400 °C [14]. A mild reduction reaction of Na₂CO₃, Mg and CCl₄ at 450 °C [15] or the reduction of hexachlorobutadiene by NaN₃ at 400 °C [16] has been reported to produce hollow carbon spheres successfully.

These earlier mentioned methods are usually involved with complicated processes or hazardous experimental conditions. Controlled preparation of nanostructures with desired shapes plays a key role in both nanomaterials science and technology. The carbon materials are known to have a different way of aggregating during reactive processes, which leads to the formation of various textures. By modification of reaction conditions and design of appropriate reaction route, it may be possible to obtain desired morphology of carbon materials. Herein, we report a convenient chemical route to shape-selectively synthesis of carbon hollow spheres, hollow capsules and solid spheres at different temperatures. These carbon materials were prepared by reduction of hexachlorobutadiene with metallic Mg powder as the reductant. The reaction system was

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conducted in an autoclave without the use of any catalyst. It is found that the shape of the carbon products and the reaction of carbon products can be controlled easily. A possible formation mechanism of the as-prepared carbon products has been proposed based on the experimental results.

Experimental

In a typical procedure, an appropriate amount of anhydrous hexachlorobutadiene (0.01 mol) and Mg (0.03 mol) were put into a glass-lined stainless steel autoclave of 50 ml capacity. The glass liner can protect the inner wall of steel autoclave from being etched by the reaction. The autoclave was sealed and maintained for 5 h at 400, 480 or 600 °C, then cooled to room temperature. After pressure relief, the autoclave was opened and product was collected. The product was washed with absolute ethanol, dilute hydrochloric acid and distilled water to remove $MgCl_2$ and other impurities. After drying in vacuum at 60 °C for 4 h, the final black powder product was obtained.

The morphology of the as-prepared samples was observed from transmission electron microscopy (TEM) images taken with a Hitachi H-800 transmission electron microscope. The high-resolution transmission electron microscopy (HRTEM) images were taken with a JEOL-2010 transmission electron microscope. Raman spectra were measured on a LABRAM-HR Raman spectrophotometer. The 5145 Å laser was used as an excitation light source. X-ray powder diffraction (XRD) pattern was carried out on a Rigaku Dmax- γ A X-ray diffractometer with Cu K α radiation (wavelength $\lambda = 1.54178$ Å).

Results and Discussion

Figure 1 shows the XRD patterns of the samples prepared at 400, 480 and 600 °C. Two prominent peaks can be found, which are indexed as the (002) and (101) reflections of the hexagonal graphite structure based on the JCPDS card (No.41-1487). The strong (002) plane peaks indicate that formation of well-ordered structure. XRD peaks are found to be a little broadened; this may be caused by a distribution of the spacing between the sp^2 carbon layers that arises from the different diameters of carbon spheres or capsules.

Further information of the sample purity and structure can be obtained from the Raman spectra. Figure 2 shows the room temperature Raman spectra of the samples prepared at 400, 480 and 600 °C. Two peaks at 1343 and 1585 cm^{-1} can be observed clearly, which are attributed to Raman D and G modes for graphite [17, 18],

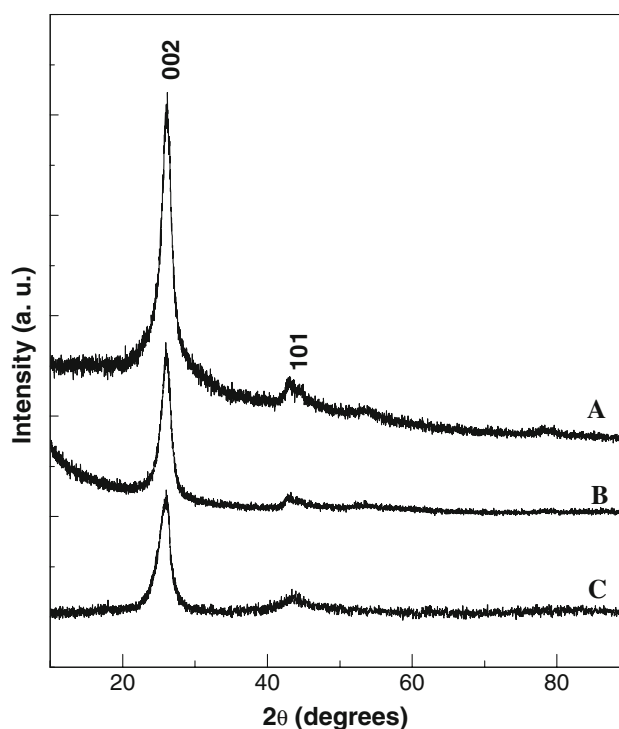


Fig. 1 XRD patterns of the as-prepared samples prepared at **a** 600 °C; **b** 480 °C; **c** 400 °C

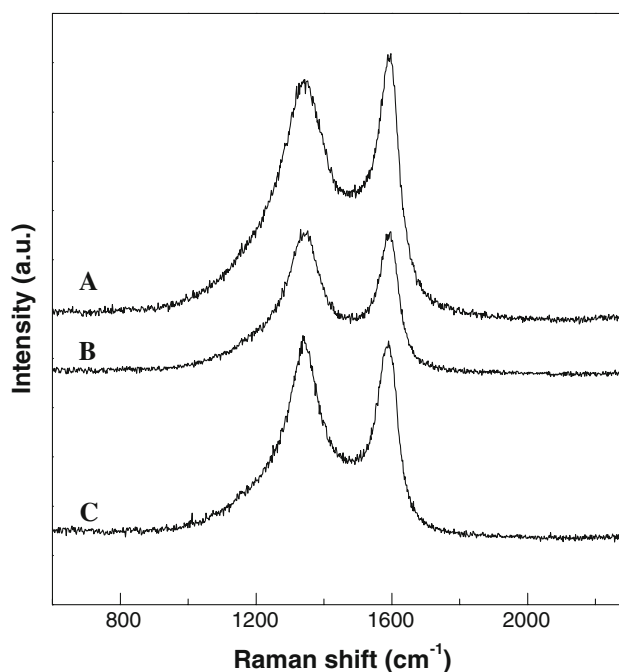
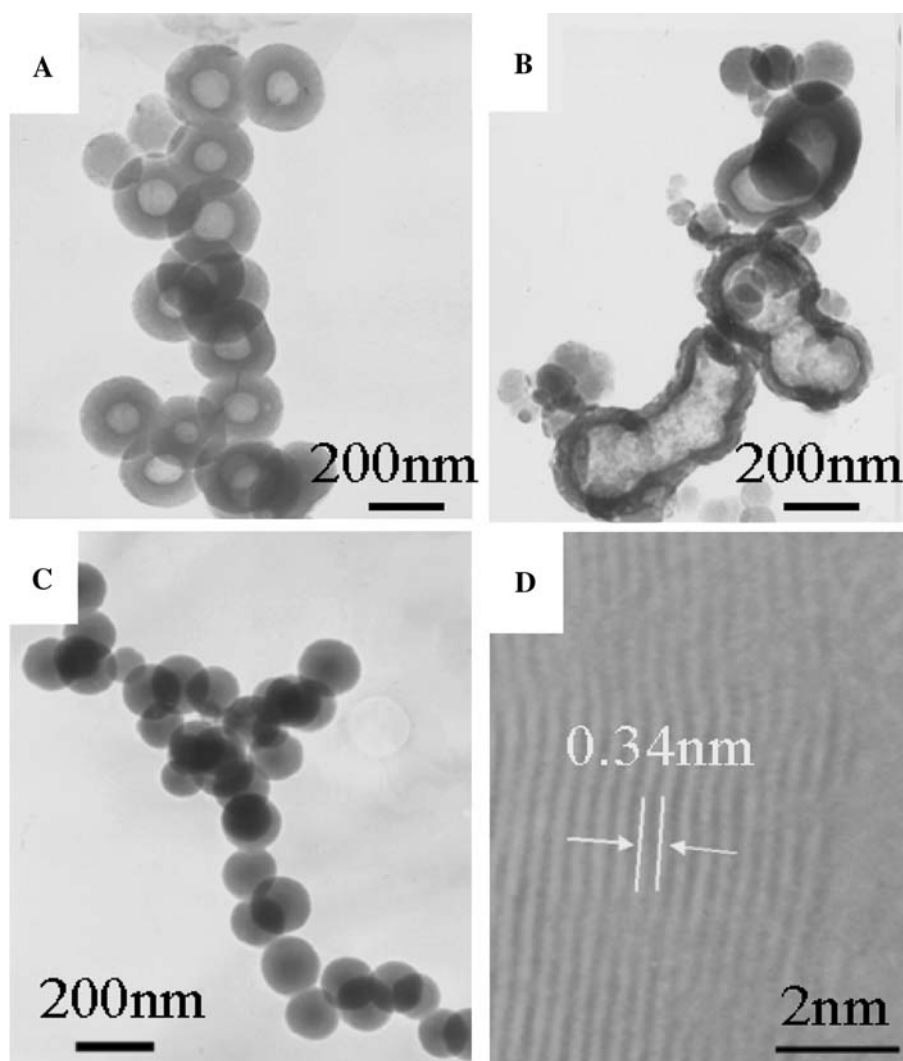


Fig. 2 Room temperature Raman spectra of the samples prepared at **a** 600 °C; **b** 480 °C; **c** 400 °C

respectively. This discloses that the as-prepared samples are all graphite structure. The 1585 cm^{-1} is associated with the vibration of sp^2 -bonded carbon atoms in a

Fig. 3 TEM images of the samples: **a** carbon hollow spheres prepared at 400 °C; **b** carbon hollow capsules prepared at 480 °C; **c** carbon solid spheres prepared at 600 °C; **d** HRTEM image of the carbon hollow capsules prepared at 480 °C



two-dimensional hexagonal lattice, such as in a graphite layer. It is worth mentioning that the relative intensity of D mode with respect to the G mode decreases gradually with increasing reaction temperature. This may be attributed to the decrease of sp^2 -bonded carbon atoms with dangling bonds, which indicates that the basal plane of the graphite structure becomes higher ordering with increasing reaction temperatures.

The morphology of the as-prepared sample was investigated by TEM. Figure 3 shows the TEM images of the samples. It can be seen from Fig. 3a that there exist hollow spheres with 300 nm average diameter in the sample prepared at 400 °C. The boundary of the hollow sphere shell is quite clear, and the shell thickness is about 50 nm. The strong contrast between the dark edge and pale center is further the proof of its hollow nature [19]. The yield of the carbon hollow spheres is estimated to be about 40–50% based on the TEM observation. Figure 3b shows the morphology of the sample prepared at 480 °C, in which the

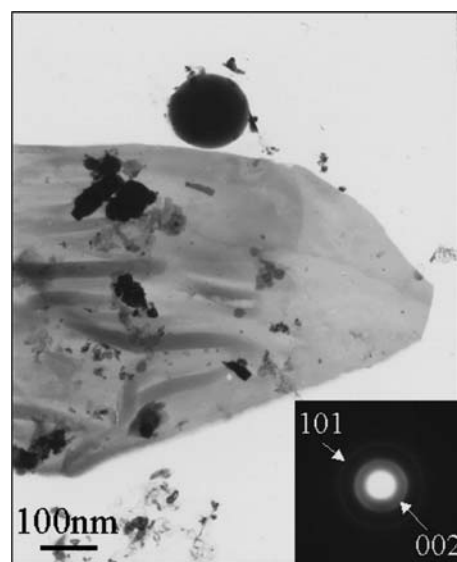
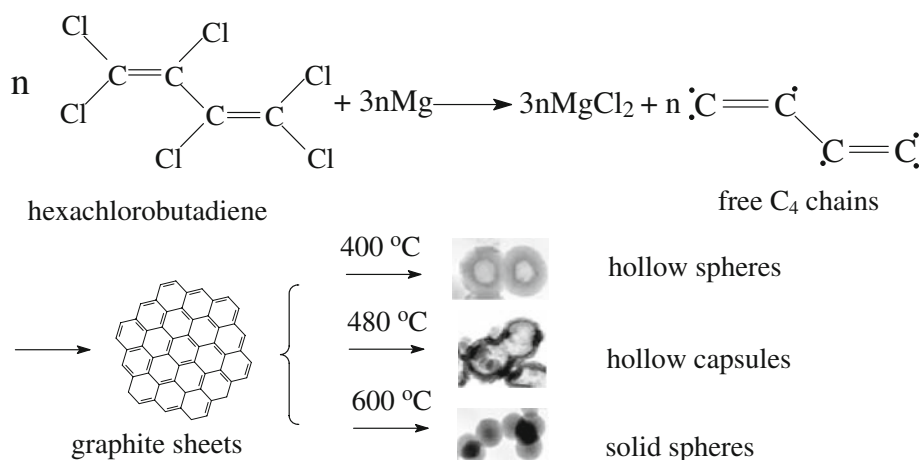


Fig. 4 TEM image and the selected area electron diffraction pattern of the graphite sheets prepared at 600 °C

Fig. 5 Illustration of the formation process of the carbon products



carbon hollow capsules can be clearly observed. The length and external diameter of the hollow capsules are about 600 and 200 nm. The thickness of the capsule shell is about 40 nm. TEM observation shows that the yield of the hollow capsules is about 35–40%. Figure 3c shows that the sample prepared at 600 °C mainly consists of carbon solid spheres, which are round, smooth and clean. The average diameter of the carbon solid spheres is about 250 nm. The yield of the carbon solid spheres is about 50–55% in the TEM observation. Direct observation for the graphite structure of the as-prepared carbon materials can be determined by HRTEM. Figure 3d shows a HRTEM image of the carbon hollow capsules prepared at 480 °C. It reveals well-resolved lattice spacing of 0.34 nm, which is in good agreement with the d spacing of the (002) planes of graphite structure.

In the process of TEM examination of the as-prepared samples prepared at 400, 480 and 600 °C, some graphite sheets can always be found, as shown in Fig. 4. The selected area electron diffraction pattern of these samples is characteristic of a hexagonal graphite structure. The rings in the pattern correspond to (002) and (101) planes. Therefore, the graphite sheet is a by-product of the reaction.

The TEM images reveal that the morphology of the samples varies with the increasing reaction temperature, which suggests that the reaction temperature plays a significant role in the morphology control. A possible mechanism for the formation of the carbon nanostructures is proposed as follows. In the experiment conducted at 400 °C, hexachlorobutadiene can be reduced continuously by Mg to. The newly formed C₄ chains are so active that they can directly react with each other to produce hexagonal lattice that is composed of sp²-bonded carbon, namely graphite sheets. This is evidenced by the observation of graphite sheets in the sample. The graphite sheets cover the Mg particles and form carbon spheres in which some

hexachlorobutadiene is also encapsulated. In the new-formed carbon spheres, hexachlorobutadiene reacts with Mg continuously and produce MgCl₂ that can be washed out by water. While the Mg is consumed completely, the hollow carbon spheres were formed. Here, the partially consumed Mg powders acted as the template; therefore, the mediate Mg powders became smaller than their initial ones. The sizes of the hollow carbon particles may not be consistent with sizes of the initial Mg powders. At a higher reaction temperature (480 °C), the hollow capsules were prepared. This suggests that more energy is needed to form hollow capsules, which may be due to larger surface strain of capsules. If the temperature is increased up to 600 °C, the solid carbon spheres were produced. The formation of a solid carbon sphere may correlate with the nucleation of a carbon ring followed by a spiral shell growth, which has been proposed to explain the formation mechanism of solid carbon spheres [20]. More energy may be needed for the formation of the spiral shell growth than that of the carbon hollow capsules. So, the reaction temperature needs to be increased further for the formation of solid carbon spheres. The details of the process for the formation of carbon hollow spheres, hollow capsules and solid spheres are still not very clear. More in-depth studies are needed. The whole process can be schematically described as follows (as shown in Fig. 5).

Conclusions

We have demonstrated a convenient chemical route to synthesize carbon hollow spheres, hollow capsules and solid spheres by Mg-reduction of hexachlorobutadiene. The morphology of the product was found to be strongly dependent on the reaction temperature. This method provides a controllable and convenient approach for the preparation of desired carbon materials without a

sophisticated technique. This approach could be further extended as a possible route to construct other desired carbon structures.

Acknowledgments The financial support of this work by the National Natural Science Foundation of China (Grant No. 20771096) and the 973 Project of China (no. 2005CB623601) is gratefully acknowledged.

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